Nitrogen Depletion Behavior of High-Nitrogen Oxynitride Films
After Reoxidation with O\textsubscript{2} and N\textsubscript{2}O Treatment

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Abstract

We investigated the nitrogen depletion behavior of high nitrogen oxynitride after O\textsubscript{2} or N\textsubscript{2}O reoxidation in a rapid thermal furnace. We observed that the nitrogen concentration decreased in both cases, and the nitrogen distribution moved toward the SiO\textsubscript{2}/Si interface when under N\textsubscript{2}O reoxidation, however, when under O\textsubscript{2} reoxidation it moved toward the surface of the SiO\textsubscript{2}.

Keywords: oxynitride, rapid thermal oxidation, nitrogen depletion, nitrous oxide, reoxidation

1. Introduction

At present the development of reliable gate insulator materials in ultra-large scale integration (ULSI) devices still requires oxynitride under mass-production, with usually a high-nitrogen concentration required in the oxynitride. This method provides a fairly reliable and high dielectric constant [1]-[3]. Various methods have been used to produce these dielectric films, such as decoupled plasma nitridation (DPN) [3], remote plasma nitridation (RPN) [4], Jet Vapor Deposition (JVD) [1] and reoxidation of NH\textsubscript{3} nitridation [2]. All of these methods require reoxidation with O\textsubscript{2} or N\textsubscript{2}O in order to obtain a high reliable gate dielectric. However, it is well know that the reoxidation step changes the nitrogen distribution and changes the concentration in the low contained-nitrogen oxynitrides (<4 at. %) [5]-[7]. There are few studies available in the literature on the reoxidation of high-nitrogen oxynitrides (>10 at.%).

In this paper we report on the reoxidation of high-nitrogen oxynitrides (12 at. %, as shown in Fig. 1) with O\textsubscript{2} or/and N\textsubscript{2}O oxidants through the rapid thermal oxidation (RTO) process.

2. Experiment

First, the oxynitride films were grown on 200 mm P-type (100) Si wafers with a resistivity of 8-12 (\(\Omega\)-cm). The wafers were cleaned by standard RCA, and dipped in HF (Hydrofluoric Acid). They were then loaded into the LIQUOZON ozonated water delivery system, made by the MKS company, to grow a layer of chemical oxide. The chemical oxide was 0.7 nm thick. Then, the chemical oxide was nitrided in pure NH\textsubscript{3} (flow rate of 1900 sccm, pressure of 1.5 Torr) in an LPCVD system at 800\textdegree C for 60 minutes, to form a 1.3-nm-thick high-nitrogen oxynitride film. Samples were then reoxidized at 1000\textdegree C in RTO with N\textsubscript{2}O (60s, 2SLM) and O\textsubscript{2} (90s, 2SLM) for periods of time as shown in table I. In table I the even number samples are stopped at N\textsubscript{2}O reoxidation except for sample 12 which is stopped at O\textsubscript{2} reoxidation, and the odd number samples are stopped at O\textsubscript{2} reoxidation. The nitrogen profiles were measured by secondary-ion-mass spectrometry (SIMS) after
each reoxidation step.

3. Results and Discussion

Figure 1 shows that the nitrogen distribution for each sample and sample 1 is the initial oxynitride with a nitrogen concentration at 12 at. %. Figure 2, which extract form figure 1, is the position of concentration of nitrogen peak relative the surface of oxynitride. Figures 1 and 2 present several phenomena: (1) the nitrogen concentration decreases gradually with the duration of the reoxidation, meaning that the nitrogen will be depleted in N₂O or/and O₂ under RTP. (2) after thermal treatment, the nitrogen peak in the N₂O is far below the surface of the oxynitride, while in O₂ it is towards the surface of the oxynitride. (3) during the N₂O reoxidation the nitrogen concentration is much more reduced than during the O₂ treatment.

In general a remarkable nitrogen depletion phenomenon occurs in oxynitride during N₂O reoxidation, but not in O₂ [7], [8]. The nitrogen depletion during O₂ reoxidation was observed by J.-J. Ganem [6] et. al., but he applied the nuclear reactions analysis (NRA). In addition, J.-J. Ganem also observed nitrogen distribution moving towards the surface during reoxidation with O₂, and he proposed that the origin of this drift was due to a concentration gradient of defects.

The finding that nitrogen distribution after reoxidation in N₂O is near the oxynitride/Si interface is in agreement with previous observations [5], [8], [9]. It is well known that nitrogen depletion is due to the fact that the atomic oxygen has broken the N-O bond which existed in oxynitride, and the NO reaction with Silicon forms a nitrogen distribution near the oxynitride/Si interface.

4. Discussion

We have developed a new method for investigating the reoxidation of oxynitride with O₂ or/and N₂O. The nitrogen depletion in the oxynitride during O₂ or/and N₂O reoxidation was evident, as was the nitrogen distribution moving towards the surface of the oxynitride during O₂ reoxidation, and near the oxynitride/Si interface during N₂O reoxidation.

References


Table 1 The process for each sample

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Figure 1 SIMS for nitrogen concentration of each sample

Figure 2 The position of the nitrogen peak value for each sample relative the surface of oxynitride